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CHARACTERISTICS ON DENSITY, MICROSTRUCTURE
AND LOW TEMPERATURE OXIDATION BEHAVIOR OF A
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MICROSTRUCTURE AND LOW
TEMPERATURE OXIDATION
BEHAVIOR OF A Si₃N₄ - 8 w/o
Y₂O₃ CERAMIC**

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NASA

EFFECT OF STARTING POWDER CHARACTERISTICS ON DENSITY, MICRO-
STRUCTURE AND LOW TEMPERATURE OXIDATION BEHAVIOR OF A
 Si_3N_4 - 8 w/o Y_2O_3 CERAMIC

by Susan Schuon and Sunil Dutta

SUMMARY

E-490 The densification and oxidation behavior of Si_3N_4 - 8 w/o Y_2O_3 prepared from three commercial starting powders were studied. Bars of SN 402, SN 502, and CP 85/15 were sintered for 3 to 4.5 hours at 1750°C . A second set was hot-pressed for 2 hours at 1750°C . The microstructures were studied by TEM and SEM, densities were determined, and the phase compositions were determined by x-ray diffraction.

Densification and microstructure were greatly influenced by the starting powder morphology and impurity content. Although SN 402 exhibited the maximum weight loss, the highest sintered and hot-pressed densities were obtained with this powder.

All powders had both equiaxed and elongated grains. Sintered bars were composed of beta silicon nitride and n-melilite. In contrast, hot-pressed bars contained beta silicon nitride, H-phase, and J-phase, but no melilite. Yttria distribution in sintered bars was related to the presence of cation impurities such as Ca, Fe, and Mg.

A limited oxidation study at 750°C in air showed no instability in these Si_3N_4 - 8 w/o Y_2O_3 specimens, regardless of starting powder.

INTRODUCTION

The inability of Si_3N_4 powder to readily sinter has led to the use of sintering additives such as MgO and Y_2O_3 . These additives promote the

formation of a liquid phase, thus enabling the Si_3N_4 powder to be sintered to a high density. Si_3N_4 - 8 w/o Y_2O_3 is considered to be one of the most promising compositions.¹ For example, commercial hot-pressed Si_3N_4 - 8 Y_2O_3 (NCX-34*), exhibits good strength and creep resistance at elevated temperatures (1300 to 1400°C).

As a general rule, the strength of a ceramic increases with increasing density. In this study, the effects of Si_3N_4 starting powder morphology and cation impurity level on the densification of Si_3N_4 - 8 Y_2O_3 ceramics was investigated for three commercial Si_3N_4 powders. Densification processes evaluated included both pressureless sintering and hot pressing. Since cracking and severe oxidation have been observed in some lots of NCX-34 at 600 to 900°C^{2,3}, the oxidation behavior of Si_3N_4 - 8 - Y_2O_3 ceramics prepared in this study was evaluated at 750°C.

EXPERIMENTAL PROCEDURE

Three commercial powders, SN 402**, SN 502**, and CP 85/15*** were selected for this study. Eight w/o Y_2O_3 was added to all three powders. Batches of 100 grams were wet milled in polyethylene bottles for 17 hrs using alumina balls and ethanol. The alumina pick up was less than 1 w/o for a 200 gram ball charge with a 100 gm powder charge. After milling, the slurry was dried on a heated aluminum plate and sieved through a 60 mesh sieve to break up agglomerates.

To make pressureless sintered specimens, twenty gram portions of mixed powder were cold formed into rectangular blocks of 7.6 by 2.5 by 0.64 cm. by

* Norton Company hot pressed Si_3N_4 - 8 Y_2O_3

** GTE Sylvania, Towanda, PA

*** KBI, Reading, PA

die pressing. The compacts were then isostatically pressed in rubber bags at a pressure of 414 MPa. The isostatically pressed bars were then sintered in a cold-wall furnace equipped with tungsten heating elements. The sintering was conducted at 1750°C for 3 to 4.5 hrs under a nitrogen pressure of one atmosphere. After sintering, the compacts were furnace cooled and weighed.

For hot pressing, eighteen gram portions of mixed powder were placed in a graphite die coated with boron nitride. Hot pressing was carried out at 1750°C for 2 hrs in one atmosphere of nitrogen under a hydraulically applied load of 276 MPa. After hot pressing the compacts were furnace cooled.

Both the sintered and hot pressed blocks were machined into test bars 2.54 by 0.64 by 0.32 cm. The bars were ground with a 220 grit diamond wheel to a final surface finish of 8-10 microinches rms.

Densities were determined on the machined test bars by physical as well as by pycnometric methods. Microstructural characterization was done by optical microscopy and by scanning and transmission electron microscopy, while phase analysis was carried out by X-ray diffraction. Yttria distribution was determined by scanning transmission electron microscopy.

The stability of hot pressed specimens at intermediate temperatures was studied. Machined test bars 2.54 by 0.64 by 0.32 cm were heated in air at 750°C. After 200 hrs at temperature, the bars were weighed and the oxide scales were characterized by X-ray diffraction.

RESULTS AND DISCUSSIONS

Powder Characterization

Commercially available Si_3N_4 powders vary considerably in particle size, particle shape, phase composition and impurity levels. The morphologies and crystallinity of the powders for the present study are shown in Figure 1.

SN 402 powder was totally amorphous. SN 402 powder particles are spherical and often agglomerated, with individual particles sizes ranging from 0.05 to 1.0 μm . SN 502 powder was about 60 percent crystalline and 40 percent amorphous, as shown in Figure 1(b). The amorphous fraction consisted of rounded particles ranging from 0.05 to 1.0 μm as in SN 402, while the crystalline fraction consisted of acicular particles with diameters ranging from 0.03 to 0.05 μm and with variable lengths. The crystalline fraction of the powder contained about 95 percent $\alpha\text{-Si}_3\text{N}_4$ and 5 percent $\beta\text{-Si}_3\text{N}_4$. In contrast, CP 85/15 powder was totally crystalline and consisted mostly of angular particles ranging in diameter from 0.05 to 6.0 μm (Figure 1(c)). Particles were about 85 percent $\alpha\text{-Si}_3\text{N}_4$ and 15 percent $\beta\text{-Si}_3\text{N}_4$.

Oxygen contents and impurity levels of the three commercial Si_3N_4 powders also varied considerably. While SN 402 and SN 502 powders had low levels of cation impurities as shown in Table 1, CP 85/15 had relatively high levels of impurities such as Al, Ca, and Fe. The oxygen contents of the SN 402, SN 502 and CP 85/15 were 2.66 percent, 2.17 percent and 1.75 percent, respectively, compared with a theoretical oxygen content for $\text{Si}_3\text{N}_4 - 8 \text{ w/o } \text{Y}_2\text{O}_3$ of 1.70 percent. Hot pressed NCX-34 has cation impurity levels similar to those determined for SN 502 powder, except for high tungsten levels, 1 to 2 w/o, in NCX-34.⁴

The BET surface areas of the three starting powders were 11.84 m^2/gm for SN 402 powder, 4.83 m^2/gm for SN 502 powder, and 3.95 m^2/gm for CP 85/15 powder.

Cold-Isostatic Pressing

Prior to sintering, SN 402, SN 502, and CP 85/15 powder mixes were cold-isostatic pressed (CIP) at 483 MPa. The lowest CIP density, 1.4 gm/cc, was obtained with the amorphous SN 402 powder, which consisted of spherical particles. The CIP density of SN 502 powder was 1.5 gm/cc, slightly higher than

that of SN 402. The highest CIP density, 2.2 gm/cc, was obtained with CP 85/15 powder, which consisted of angular, platy particles. The densities are plotted in Figure 2.

Each type of CIP bar had a distinctive fracture surface, which reflected starting powder morphology as shown in Figure 3. In SN 402 and SN 502 bars, individual particles are distinguishable, indicating a large amount of open porosity. In contrast, the individual particles are somewhat difficult to distinguish in CP 85/15 fracture bars due to greater mechanical agglomeration and more numerous particle contacts.

Densification

Sintering

The CIP bars were sintered in nitrogen for 3 hours or 4.5 hours at 1750°C. After 3 hours, the density of SN 402 bars increased from about 1.4 gm/cc to about 1.8 gm/cc, as shown in Figure 2. The density of SN 502 bars increased from 1.55 gm/cc to 1.90 gm/cc. On the other hand, the density of CP 85/15 bars decreased slightly during sintering, from 2.0 gm/cc to 1.95 gm/cc. This decrease in density was also observed by Galasso and Veltri³.

Sintering for 4.5 hours did not improve the final densities of CP 85/15 and SN 502 bars. However, longer sintering time did increase the density of SN 402 CIP bars, from about 55 percent of the theoretical density of 3.28 gm/cc to about 94 percent theoretical density. In comparison, NCX-34, which is hot pressed, has a density of about 98 percent of theoretical.

The results were not in accord with the general rule that the higher the green density, the higher the final density of the end product. For example, SN 402 powder exhibited the lowest green density (1.4 gm/cc) but also exhibited the highest sintered density (3.1 gm/cc). CP 85/15 powder had the highest

green density (2.0 gm/cc), but exhibited a slight decrease in sintered density (to 1.85 gm/cc). These observations suggest that densification of Si_3N_4 powder compacts depends more on the powder reactivity than initial green density. The higher surface area of the SN 402, about twice that of the other powders, provided greater reactivity and enhanced sintering. However, in all cases, densification was facilitated by formation of a liquid phase with Y_2O_3 at the sintering temperatures.

Weight loss

Substantial weight losses occurred on sintering at 1750°C. SN 402 bars had the maximum weight loss, about 21 percent of their green (CIP) weight; SN 502 bars had a loss of about 6.4 percent, while the weight loss in CP 85/15 bars was about 10.2 percent. However, SN 402 bars, in spite of having the highest weight loss, sintered to the highest final density. On the other hand, SN 502 bars had minimum weight loss but sintered to the lowest final density. The large weight loss in SN 402 bars during sintering is attributed to thermal decomposition of amorphous, submicron, Si_3N_4 particles at the external surface of the bars.

Hot pressing

The three Si_3N_4 powder types were hot pressed at 1750°C for 2 hrs in one atmosphere of nitrogen under an applied pressure of 276 MPa. The purpose of hot pressing was (1) to determine the maximum densities that could be achieved with different types of Si_3N_4 starting powders for comparison with sintered products, and (2) to prepare high density samples for study of the intermediate temperature oxidation behavior. The densities of all three powders hot

pressed for 2 hrs at 1750°C are compared with the densities of samples sintered for 3 hrs at 1750°C in Figure 4. The highest density (3.2 gm/cc) was observed in SN 402 powder followed by CP 85/15 (3.05 gm/cc) and SN 502 powder (2.75 gm/cc). In all cases, the hot pressed densities were significantly higher than the sintered densities, confirming the advantage of hot pressing for achieving high density ceramics.

Microstructure

The microstructures of both sintered and hot pressed Si_3N_4 bars were examined by transmission and scanning electron microscopy. These microstructures are shown in Figures 5 to 8. All Si_3N_4 bars had duplex grain structures containing both equiaxed and elongated grains. Approximate grain size ranges and aspect ratios are listed in Table 2.

The sintered SN 402 bar had a large population of equiaxed grains 0.05 to 0.5 μm in diameter and a small population of elongated grains 0.5 to 10.0 μm in length. The grain size range of sintered CP 85/15 bars was found to be uniform (Figure 5(c)). Both equiaxed and elongated grains were less than 1 μm in width.

Hot pressed SN 402 bars, shown in Figure 6(a), had finer grains than did sintered SN 402 bars. On the other hand, hot pressed SN 502 and CP 85/15 bars had grain size ranges which were approximately equivalent to those of sintered bars. Of the three different types of powders, the fully crystalline CP 85/15 powder exhibited the most uniform grain size.

The fracture surfaces of samples sintered for 3 hrs are shown in Figure 7. These samples had a partially developed grain structure with interconnected pores, consistent with their intermediate densities as shown in Figure 2. In comparison, fracture surfaces of hot pressed samples, shown in Figure 8,

have more or less well developed grain structure with disconnected pores, typical of high density structures associated with more complete sintering.

Phase determinations on sintered and hot pressed bars were done by X-ray diffraction. Differences in phase composition were found between sintered and hot-pressed bars. Sintered bars, regardless of starting powder, contained β - Si_3N_4 , n-melilite ($\text{Y}_2\text{Si}_3\text{N}_4\text{O}_3$) and a vitreous phase SN 502 and CP85/15 hot-pressed bars contained β - Si_3N_4 , H-phase ($\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$), and J-phase ($\text{Y}_4\text{Si}_2\text{O}_7$), while SN 402 hot-pressed bars contained β - Si_3N_4 and other secondary phases. Limited observations indicated that these phases are also found in NCX-34.⁴

The microchemical segregation of yttria, the sintering aid, was found to vary with the cation impurity content of the three starting powders possibly due to lowering of the melting point of yttria phase by the impurities. As shown in Figure 9, CP 85/15 sintered powder, which had the highest cation impurity content, had the greatest yttria segregation (Figure 9(c)) while SN 402 sintered powder, with the lowest cation impurity content, had a very uniform yttria distribution (Figure 9(a)).

Oxidation in Air at 750°C

After 200 hours continuous exposure at 750°C, no cracking or scaling was observed in hot-pressed SN 402, SN 502, or CP 85/15 bars as shown in Figure 10(a). Weight gain after 200 hours was negligible. These results are in contrast to the observations by Brennan⁵, who reported severe cracking and oxidation of a similar Si_3N_4 - Y_2O_3 ceramic, NCX-34, during exposure to air at 750°C for 48 hours, as shown in Figure 10(b). This instability in NCX-34 has been attributed to carbon contamination⁶ or tungsten contamination⁷ during milling. In contrast, no tungsten contamination was observed in the materials of this study. Only a small amount of cristobalite was detected in

the surface of the SN 502 bar. Cristobalite was not observed on the SN 402 and CP 85/15 bars.

CONCLUDING REMARKS

The experimental work reported in this study has shown that significant differences exist in particle size, particle shape, and impurity content of three commercially available silicon nitride powders. Sintered densities approaching 3.1 gm/cc (95 percent of theoretical) were obtained only with the amorphous SN 402 powder; this high density was attributed to the high surface area nature of the powder. On the other hand, the presence of cation impurities such as Ca, Fe and Mg in fully crystalline CP 85/15 powder did not promote significant densification during sintering. The amorphous powder (SN 402) exhibited a greater weight loss than the other powders; this was probably due to the greater surface area of the 402 powder and the associated thermal decomposition of amorphous, submicron particles at the external surface of the compacts. Duplex grain structures were observed in both sintered and hot pressed materials.

In a limited oxidation study, no instability was observed in hot pressed $\text{Si}_3\text{N}_4 - 8 \text{ w/o } \text{Y}_2\text{O}_3$ prepared from three different commercial powders (SN 402, SN 502, CP 85/15) and exposed in air at 750°C.

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3. F. S. Galasso and R. D. Veltri, "Sintering of Si_3N_4 Under Nitrogen Pressure," Army Materials Research Agency, Watertown, MA, AMMRC TR 79-37, June 1979. AD-A072515.
4. D. C. Larsen, "Property Screening and Evaluation of Ceramic Turbine Engine Materials," Air Force Materials Lab., Wright-Patterson AFB, OH, AFML-TR-79-4188, October 1979. AD-A080963.
5. J. J. Brennan, "Development of Silicon Nitride of Improved Toughness," United Technologies Research Center, East Hartford, CT, R79-914364-12, October 1979. NASA CR-159676.
6. H. Knoch and G. E. Gazza, "Carbon Impurity Effect on the Thermal Degradation of a $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ Ceramic," Army Materials Research Agency, Watertown, MA, AMMRC-TR-79-27, May 1979. AD-A075138.
7. S. R. Schuon, "Effect of W and WC on the Oxidation Resistance of Yttria-doped Silicon Nitride," NASA TM-81528.

Table 1. Trace Element Impurity Analysis
of Silicon Nitride Powders.

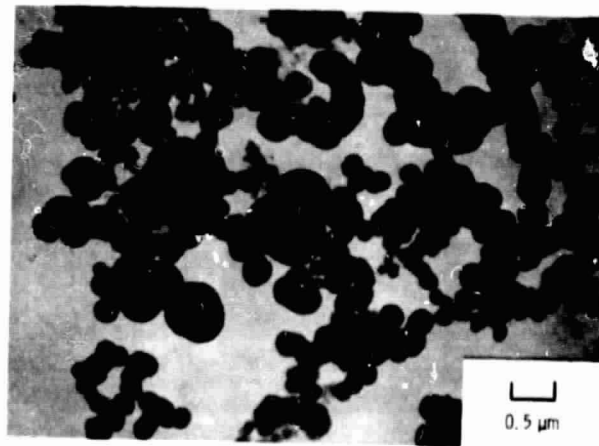
Impurity Element Content, ppm

<u>Element</u>	<u>SN 402</u>	<u>SN 502</u>	<u>CP 85/15</u>
Al	<30	50	3000
C	(a)	410	2600
Cu	<30	50	140
Ca	<30	130	3000
Cr	<30	30	200
Fe	70	30	3000
Mg	<30	110	140
Mn	<30	(a)	260
Mo	<30	80	300
O	26600	21700	17500
Ti	<30	40	530
Zr	<30	100	180

(a) Not analyzed

Table II - Grain Size Ranges and Aspect Ratios of
Hot-Pressed and Sintered Si₃N₄ - 8 w/o Y₂O₃

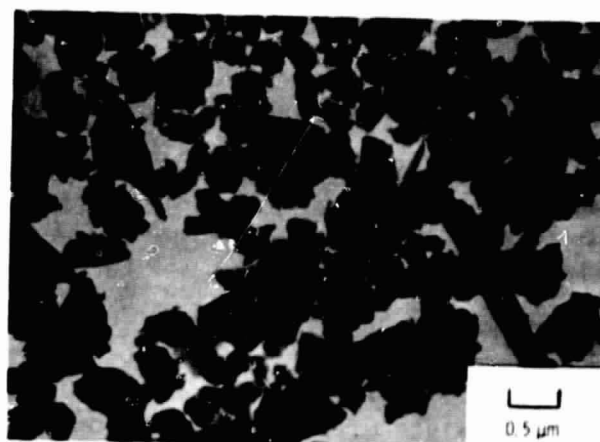
	Hot Pressed	Sintered
SN 402	Small grains 0.05 - 0.5 μ m; aspect ratio, 1:2.5 to 1:5 Large grains usually elongated, width 0.5 to 1.5 μ m; aspect ratio 1:3 to 1:5.	Small grains, 0.05 - 0.3 μ m; aspect ratio, 1:2.5 to 1:5. Large grains equiaxed, 0.5 to 10.0 μ m.
SN 502	Equiaxed, 0.1 to 10.0 μ m; elongated, width 0.12 to 1.2 μ m aspect ratio 1:3 to 1:5.	Equiaxed 0.15 to 10.0 μ m; elongated, width 0.2 to 0.8 μ m; aspect ratio 1:2 to 1:4
CP 85/15	Equiaxed, 0.15 to 0.6 μ m; elongated, width 0.3 to 1.0 μ m, aspect ratio, 1:2.5 to 1:4	Equiaxed, 0.2 to 0.6 μ m; majority elongated grains, width 0.1 to 0.4 μ m, aspect ratio 1:2 to 1:4



(a) SN402.



(b) SN502.



(c) CP8515.

Figure 1 - Transmission electron micrographs of three commercial silicon nitride powders

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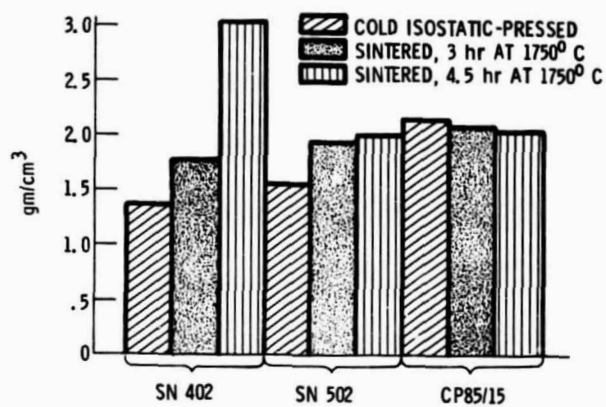
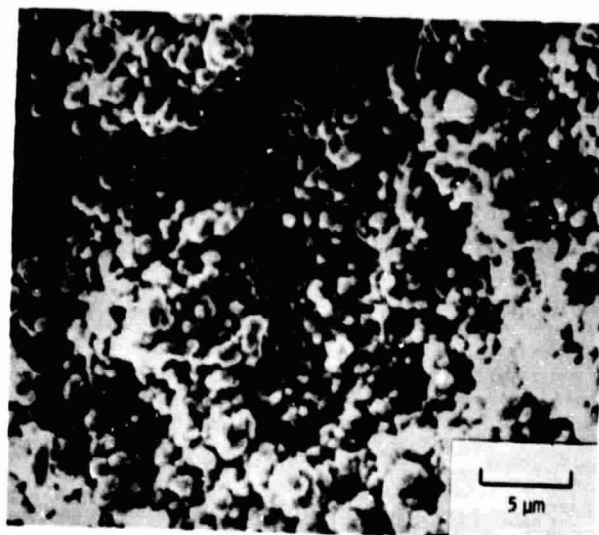
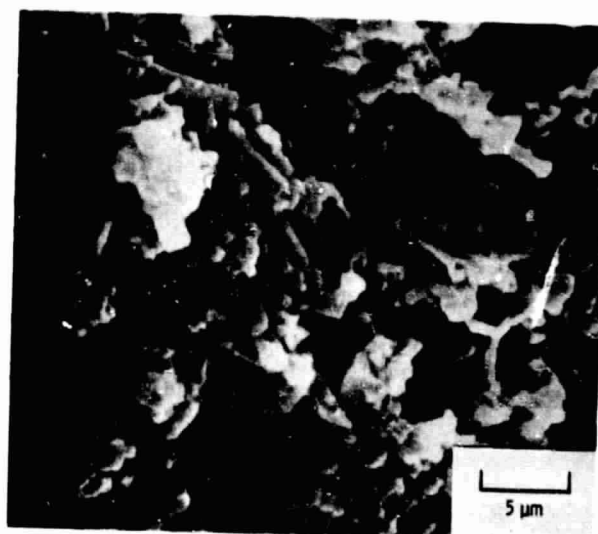


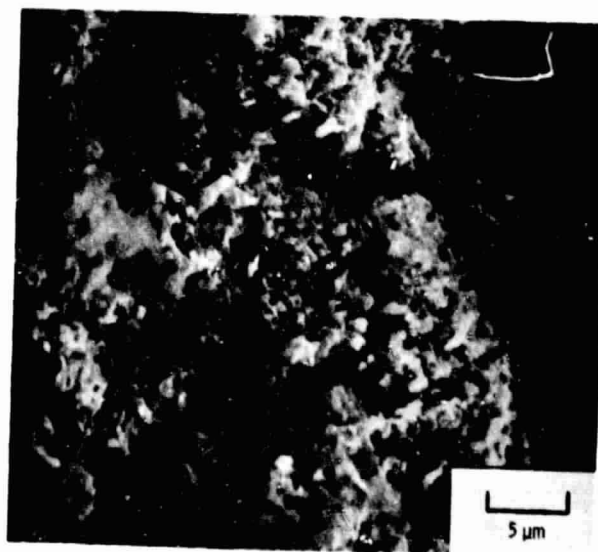
Figure 2. - Density of silicon nitride + 8w/o yttria cold isostatically-pressed (CIP), sintered for 3 hrs at 1750°C (3h), and sintered for 4.5 hrs at 1750°C.



(a) SN402.



(b) SN502.



(c) CP85/15.

Figure 3. - Fracture surface of cold-isostatically pressed $\text{Si}_3\text{N}_4 + 8 \text{ w/o } \text{Y}_2\text{O}_3$

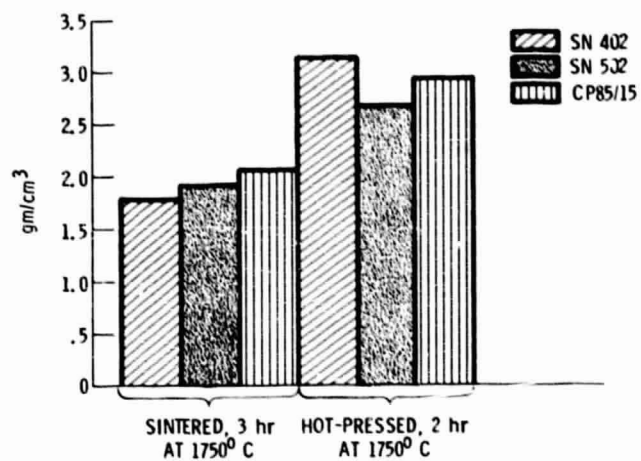
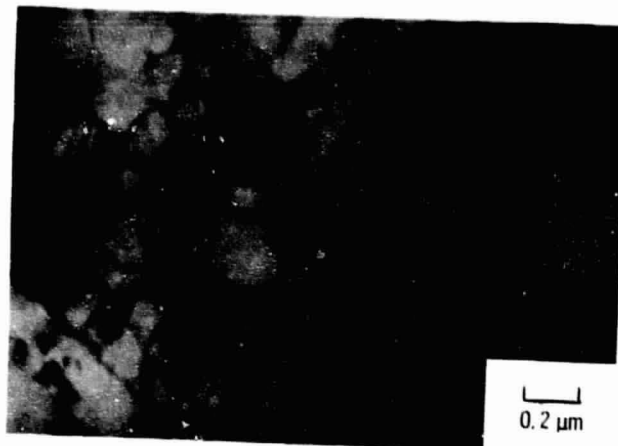
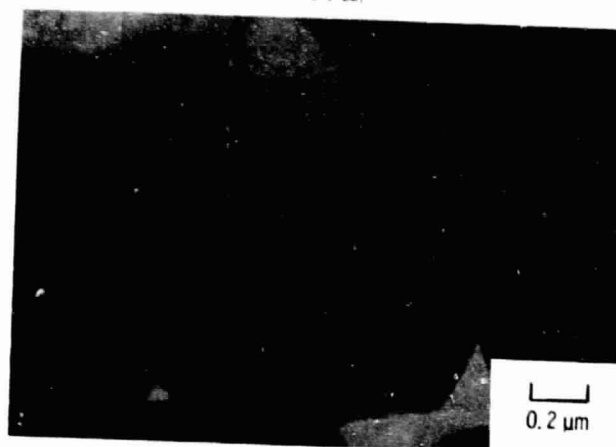


Figure 4 - Density comparison of silicon nitride + 8w/o yttria sintered (S) for 3 hrs at 1750° C and hot-pressed (HP) for 2 hrs at 1750° C.



(a) SN402.



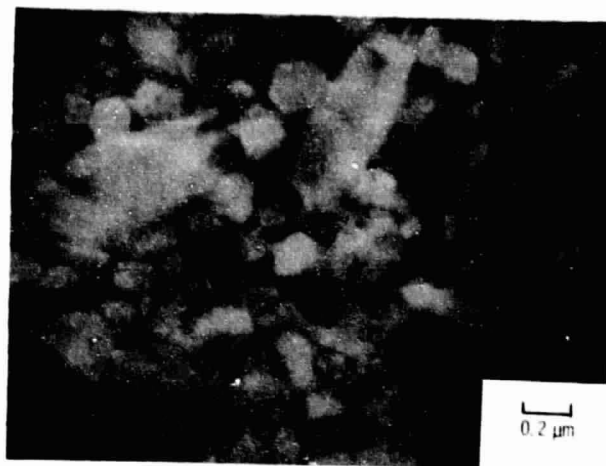
(b) SN502.



(c) CP85/15.

Figure 5. - TEM of silicon nitride + 8 wt% Y_2O_3 sintered for 3 hours at 1750°C.

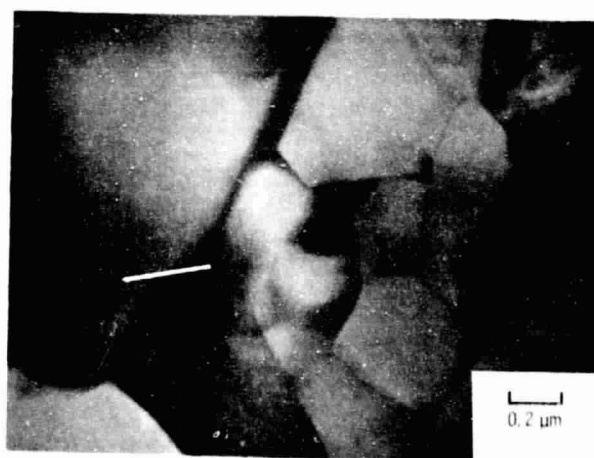
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(a) SN402

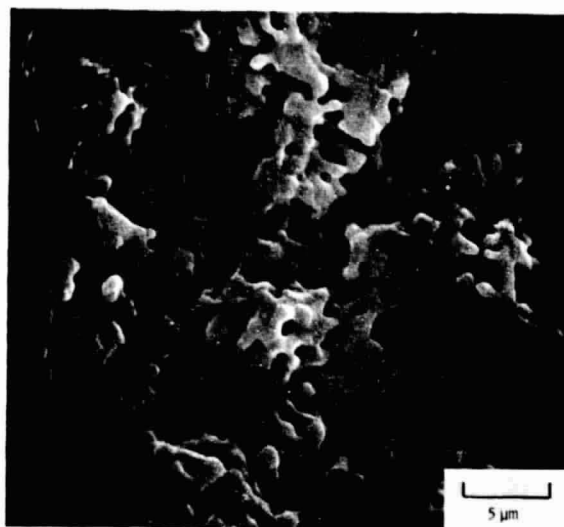


(b) SN502



(c) CP85-15

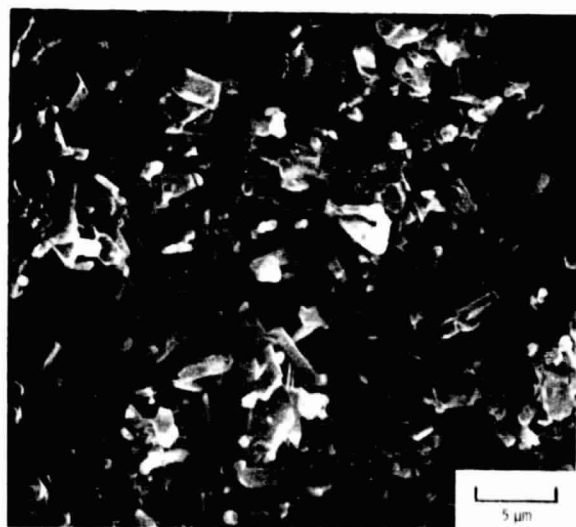
Figure 6 - TEM of $\text{Si}_3\text{N}_4 + 8 \text{ wt } \% \text{Y}_2\text{O}_3$ hot-pressed for 2 hours at 1750°C



(a) SN402.

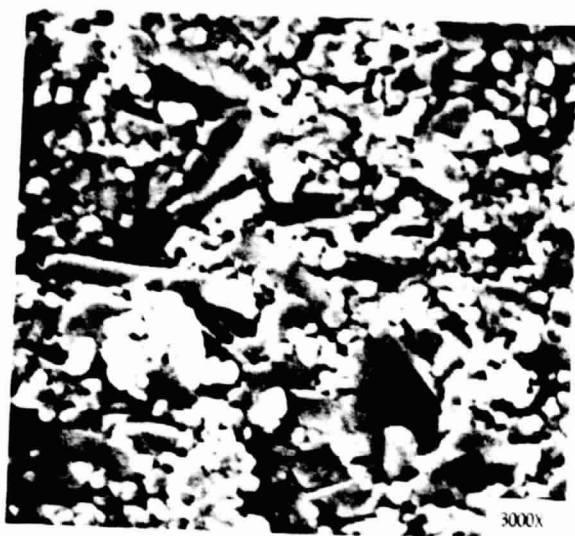


(b) SN502.



(c) CP85-15.

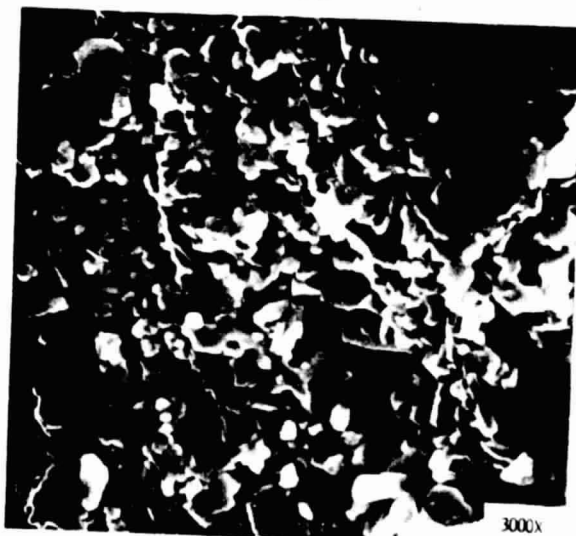
Figure 7. — Fractograph of $\text{Si}_3\text{N}_4 + 8 \text{ w/o } \text{Y}_2\text{O}_3$ sintered for 3 hours at 1750°C



(a) SN402



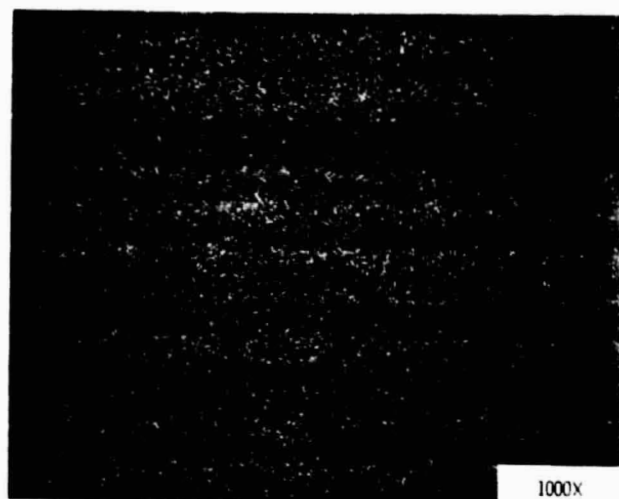
(b) SN502



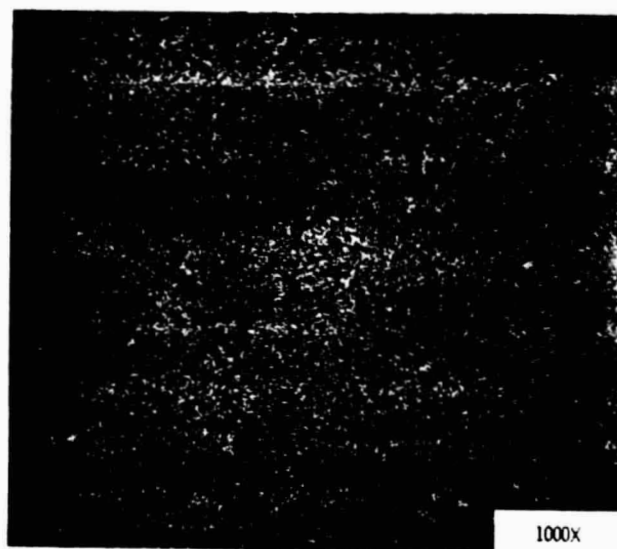
(c) CP85-15

Figure 8 - Fractograph of $\text{Si}_3\text{N}_4 + 8 \text{ w/o } \text{Y}_2\text{O}_3$ hot-pressed for 2 hours at 1750°C

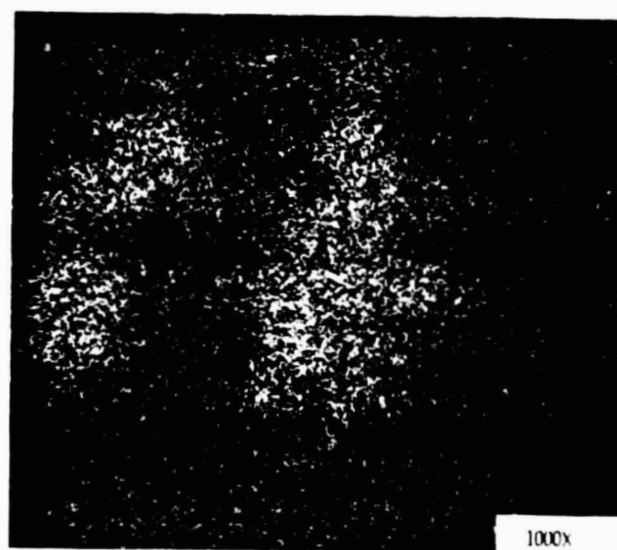
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(a) SN402.

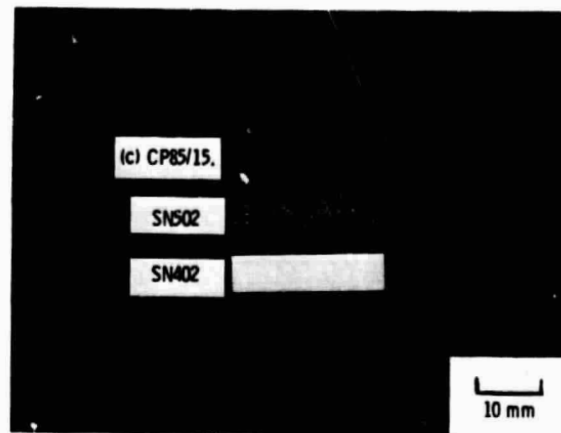


(b) SN502.

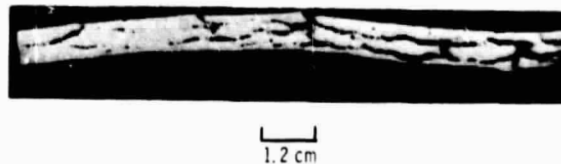


(c) CP85/15

Figure 9 - Microchemical distribution of yttrium in sintered $\text{Si}_3\text{N}_4 + 8 \text{ wt} \% \text{Y}_2\text{O}_3$ ceramics.



(a) CP85/15, SN402, SN502 AFTER 200 HR AT 750° C.



(b) NCX-34 Si_3N_4 (BILLET F338355) AFTER 48 HR AT 730° C.

Figure 10. - Three hot-pressed silicon nitride + 8 w/o yttria bars oxidized in air.

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